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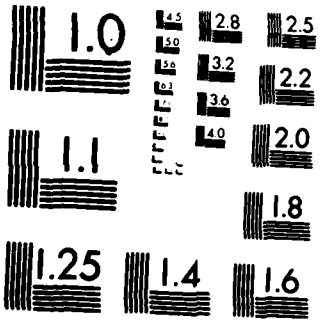

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AFOSR-TR- 86-0824

Final Report to the Air Force Office of Scientific Research

Subject: Vibrational Participation in Chemical Reactions
Nanosecond Infrared Spectroscopy

Principal Investigator: Professor George C. Pimentel
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George C. Pimentel

This report describes research progress under AFOSR Grant #82-0031 for the period November 1, 1981-October 31, 1985.

RESEARCH ACCOMPLISHMENTS include:

A. Vibrational Excitations of Reactions in Cryogenic Solids-
(Bibliographic Entries 2,5,8,9,10,11,12,14,18,21,22)

The first and, as yet, the only evidence for mode-selective excitation of bimolecular reactions has been obtained in our laboratories under AFOSR support. Many laboratories have endeavored to demonstrate mode-selective excitation of either unimolecular or bimolecular reactions since tunable lasers have come into the hands of chemists. Apparently under normal conditions, gas or liquid phase and at room temperature, intramolecular energy redistribution is so rapid that the selectivity is lost. Our success apparently can be attributed to our use of the solid inert gas environment at cryogenic temperatures (12°K) and our investigation of bimolecular reactions that can be excited with photons of sufficiently low energy that the reactant energy level diagram is still sparse. We believe that a significant, perhaps crucial, part of this technique is that rotational degrees of freedom are frozen out.

Our first system selected for study was the NO + O_3 reaction. (See ref. 2.) This study was complicated by the fact that the reaction proceeds slowly at 12°K in absence of radiation and despite the 2-3 kcal/mole activation energy. Apparently heavy atom tunnelling occurs. Even so, we were able to accelerate the reaction using tuned laser excitation of the NO stretching motion at 1874 cm^{-1}. Because of the background rate, we were not able to test for mode selectivity.

The fluorine-olefin reactions, F_2 + ethylene and F_2 + allene, provided our real successes. These reactions showed, first, that the reactions can be stimulated with tuned laser excitation of the olefin and, second, that the quantum yield is very strongly dependent on the energy of the exciting photon. For example, the quantum yield for the $F_2 + C_2H_4$ reaction was less than 10^{-6} for excitation of ν_7 at 953 cm^{-1}, almost 10^{-3} for $\nu_7+\nu_8$ at 1896 cm^{-1}, and 0.3 for the quaternary combination $\nu_3+2\nu_7+\nu_8$ at 4209 cm^{-1}. Such a monotonic rise of ϕ with ν is not mode selectivity, of course. The mode selectivity is associated with significant deviations

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from this monotonic behavior. Table I lists the examples we have measured in which there are quantum yield changes that are clearly not associated solely with the photon energy but, instead, depend upon the mode excited. The allene example in which ν_9 is about two orders of magnitude more effective that ν_6, though there is only a 46 cm^{-1} energy difference between the exciting photons is a striking case.

Table I

Quantum Yield-Frequency Anomalies Due to Mode Selectivity

	Mode	ν (cm^{-1})	ϕ
$F_2 + C_2H_4$ [a]	ν_{11}	2989	$4.3 \cdot 10^{-2}$
	$\nu_2+\nu_{12}$	3076	$7.0 \cdot 10^{-2}$
	ν_9	3105	$2.3 \cdot 10^{-2}$
F_2 + t-CHDCHD [a]	$\nu_7+\nu_8$	1588	$<2 \cdot 10^{-4}$
	$\nu_4+\nu_8$	1855	$1.1 \cdot 10^{-3}$
	$\nu_3+\nu_{10}$	1961	$<6 \cdot 10^{-4}$
	ν_9	3067	$1.3 \cdot 10^{-2}$
$F_2 + H_2CCCH_2$ [b]	$2\nu_{10}$	1679	$2 \cdot 10^{-5}$
	ν_6	1953	$<2 \cdot 10^{-6}$
	ν_9	1999	$1.4 \cdot 10^{-4}$
	ν_8	3076	$2.0 \cdot 10^{-3}$

a. reference 8
b. reference 9

A variety of additional avenues appeared that were explored. Thus the quantum yields for the dideuteroethylenes plainly revealed a symmetry effect in the phonon-induced relaxation process. The trans-$C_2H_2D_2$, with its center of symmetry, showed ten-fold higher quantum yields than either cis-$C_2H_2D_2$ or 1,1-$C_2H_2D_2$, neither of which retains the center of symmetry. A second interesting facet concerned the branching associated with the HF elimination reactions that can follow the exothermic addition of F_2 to the olefin. For C_2H_4, the stabilization of the 1,2 difluoroethane relative to the elimination product vinyl fluoride was increased one or two orders of magnitude if the cage included a second C_2H_4 molecule, apparently acting as an energy sink to cool off the reaction product. A third behavior of significant interest was the observation of mode-dependent isomerization rate for the reaction products in the F_2 + allene reaction. Both trans-and gauche- 2,3-difluoropropene were observed and, with tuned laser irradiation, either rotamer could be converted quantitatively into the other (see reference 9).

All of this work is summarized in the review article, reference 18.

Quite a difference kind of selective excitation was involved in the multiphoton excitation of trifluoroethene (ref. 14). In this case, a high power pulsed CO_2 laser is tuned to a C-F stretching mode of the C_2HF_3 which is then excited through the absorption of at least 30 quanta during the 70 nsec laser pulse. This places about 80 kcal/mole of energy in the olefin and $\alpha\alpha$ elimination occurs to produce difluoro vinylidine, F_2CC. This molecule apparently is sufficiently stable to fluorine migration that it does not isomerize to difluoroacetylene but, instead, reacts with parent olefin. Here, a surprising chemical pathway was discovered. The F_2CC molecule reacts in the gas phase with an olefin to insert a carbon atom, producing the corresponding allene and CF_2. This chemistry was verified by reaction of F_2CC with C_2H_4, C_2D_4, C_2HF_3, and C_2F_4 to produce, respectively, allene, perdeuteroallene, trifluoroallene, and perfluoroallene. This represents the first discovery of such an insertion as a means of producing substituted allenes or cyclic allenes.

Fortunately, we were also successful in detecting special chemistry of the parent olefin caused by its extremely high vibrational excitation (prior to HF elimination). Metathesis occurs when such a vibrationally hot C_2HF_3 molecule collides with a second olefin. As an example, when $C_2HF_3^{\ddagger\ddagger}$ collides with C_2H_4, the products include C_2H_3F and CF_2CH_2. This is one of the earliest examples of special bimolecular chemistry connected with multiphoton excitation. The particular metathesis reaction we have observed is relevant to catalytic metathesis of olefins, an important commercial process.

B. HF Rotational Lasers -

(Bibliographic entries 3,7,13,15,16,17,22)

One of the significant and least understood aspects of the performance of the HF chemical laser has been the role of rotational degrees of freedom in vibrational relaxation. Without this knowledge, it is not yet confident that the HF laser has been optimized. General acceptance of the importance of $\Delta v=1$ V→R relaxation stemmed from the early observation of J=14→13 HF emission by Cuellar, Parker, and Pimentel (1974, 1979) and the more decisive observations of Sirkin and Pimentel (1981, 1982, references 3 and 7) and of D.W. Robinson and coworkers who worked with the analogous molecules NH and OH (1978, 1979, 1981). This V→R process, with $\Delta v=1$ already required that large changes of the rotational quantum number take place with relative ease in a single event ($\Delta J=9$ to 14). Only our work, however, extended to sufficiently high rotational transitions (up to J=31→30) to indicate that the vibrational quantum number also might be changing by more than one. This possibility was not greeted warmly by the researchers who had labored hard to deconvolute vibrational relazation data using models in which Δv was restricted to one.

The detailed work in reference 7 showed that the group of molecules H_2, D_2, and HCl was qualitatively different in collisional relaxation properties from the group CO, CO_2 and N_2. Whereas the light-atom containing molecules quenched rotational laser emission from high J states of HF, the second group, CO, CO_2, and N_2, enhanced it and caused a number of new transitions to reach laser threshold. It was deduced that rotation-to-rotation relaxation processes

take place when the HF collision partner contains a light atom, H or D. Clearly, momentum transfer efficiency in such R→R' processes is important. With this process muted for the heavy-atom molecules like CO, it is possible to perceive the direct transfer of HF vibrational energy into HF rotational energy by such processes HF(v=3, J=3) + CO→HF(v=0, J=24) + CO, and HF(4,5) + CO →HF(0,28) + CO, neither of which is observed with argon collision partner. Also detectable were laser transitions evidently pumped by processes involving vibrational excitation of the CO collision partner, such as HF (3,0) + CO (0,0)→ HF (0,21) + CO (1,0).

This work was elegantly advanced in reference 13 through tandem laser measurements that revealed the time evolution of gain for very high J rotational laser transitions such as v=0, J=30→29, 29→28, and 28→27. In this case, the pumping reaction was H + ClF and the results showed that both R→T erosion pumping and V→R near-resonant energy transfer were active, the latter process clearly being associated with the ClF collision partner. The time evolution showed that the initial pumping reaction directly provided population to HF rotational states as high as v=0, J=30 and v=1, J=32 but that quickly the gain behavior is dominated by collisional processes dependent upon V→R energy transfer.

What remained out of reach was a quantitative estimate of the relative importance of V→R processes with $\Delta v>1$ relative to the other vibrational relaxation channels. This was finally addressed in reference 16 in which experiments were conducted using in-cavity known attenuators. With the collision partners CO and N_2 it was possible to deduce that in the vibrational relaxation of HF from the v=5 manifold, the dominant relaxation channels are V→R (including $\Delta v=1$) and that a few percent of the relaxation rate can be associated with the $\Delta v=3$ channel HF(v=5, J=3,4) + M→HF (v=2, J=24) + M. This is presently the only quantitative estimate of the rate constant for a V→R process involving both a large change in ΔJ and also $\Delta v>1$.

All of these data furnish a basis for a detailed computer modeling with more general deductions about the V→R rate constants (reference 22). This has been completed and will be reported soon.

C. Nanosecond Infrared Spectroscopy

The pioneering work of Sorokin and Bethune (1977, 1979) showed that Stimulated Electronic Raman Scattering (SERS) could extend rapid scan infrared spectroscopy to the 10 nsec time scale. One of the major activities of this grant period has been the adaptation of the Sorokin/Bethune technique to the development of a 10 nsec spectrometer that would operate in the 7 to 11 micron spectral range with one wave number spectral resolution. Our initial pump laser is an excimer laser that pumps a suitable dye laser to produce a 10 nsec ultraviolet continuum pulse. The dye laser output is focussed into a cesium vapor heat pipe in which the stimulated Raman effect produces an infrared continuum pulse of less than 10 nsec duration and in the desired spectral range.

This infrared pulse is passed through the sample under study to inscribe its characteristic infrared "fingerprint" and then into a monochrometer to disperse the light so it can be detected with an array detector. Present work involves a 120 element mercury/cadmium/telluride array cooled to liquid nitrogen temperature. Each detector element is about 50 by 50 microns in size with peak sensitivity near 11 microns. Each element has its own amplifier and "hold" circuit so that 120 analogue signals are stored after the arrival of the nanosecond infrared pulse. Then a multiplexer unit reads out the stored information, converts it to digital form for computer storage and manipulation, and clears the "hold" circuitry for the next infrared pulse.

As of this writing, this equipment is fully operative and work is beginning in its application to the detection of transient species, such as occur in explosions and flames, with lifetimes in the 10 nsec to the microsecond time domain.

Personnel: 1981-1985

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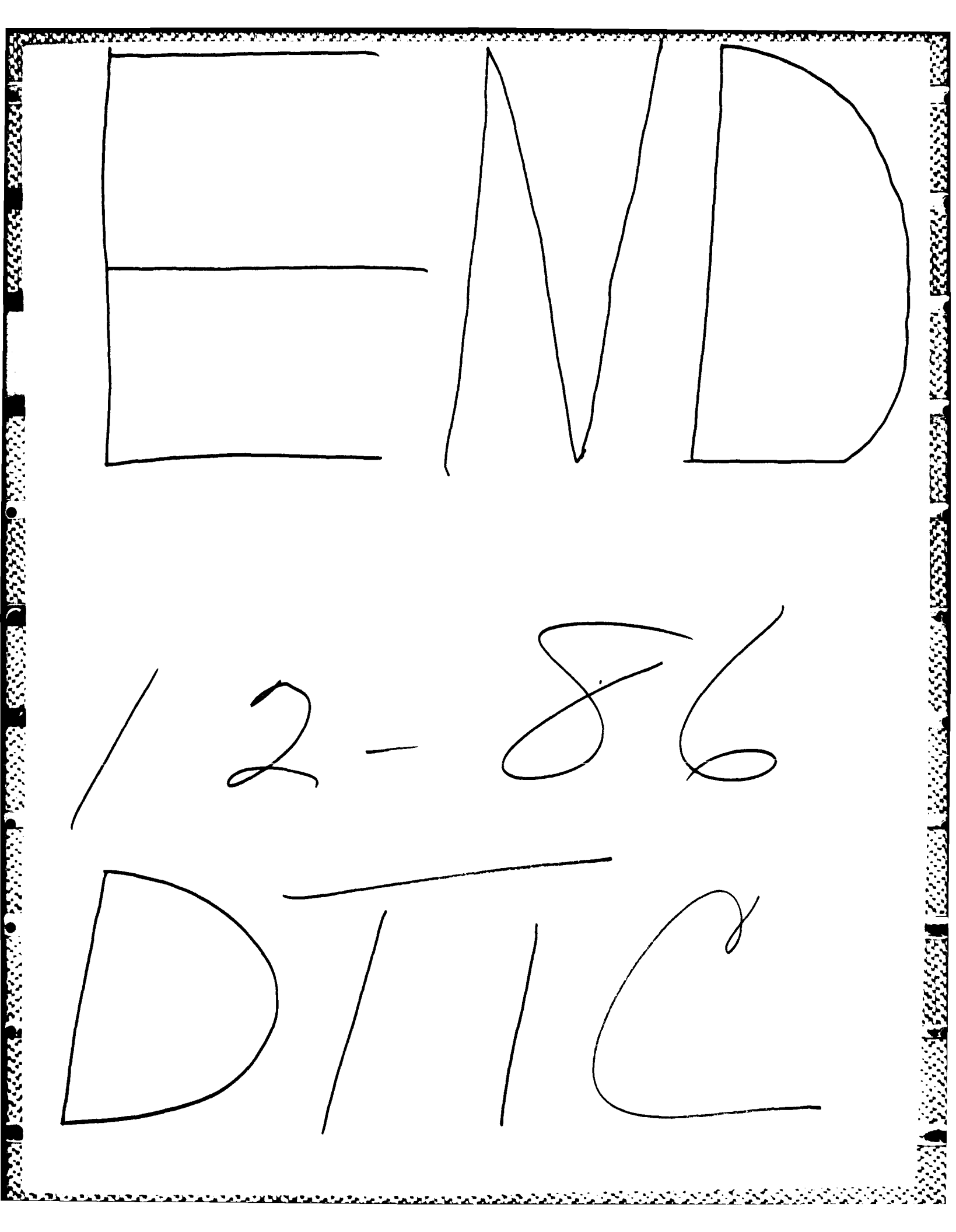
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